Indian J. Phys. **78** (11), 1221-1224 (2004)

AN INTERNATIONAL JOURNAL
IJP

Magnetic ordering in a Zn-substituted Co-Mn-Fe-O ferrite system

D R Shengule, K M Jadhav and G K Bichile*

Department of Physics, Dr Babasaheb Ambedkar Marathwada University, Aurangabad - 431 004, Mahrashtra, India

E-mail gkbichile@lycos.com

Received 21 July 2003, accepted 30 July 2004

Abstract : The structural and bulk magnetic properties of Zn-substituted $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ ($x = 0.0 - 0.6$) ferrite system are studied using X-ray diffraction, magnetization and a.c. susceptibility measurements. The X-ray intensity calculations indicate that Mn^{4+}, Co^{2+} occupy only B-sites, Zn^{2+} have strong preference for A-site and Fe^{3+} ions distributed among A and B-sites. The magnetization measurements exhibits a significant canting on the B-site which is satisfactorily explained on the basis of the non-collinear spin model of uniform canting. The a.c. susceptibility indicates that system orders into a cluster spin glass state with the magnetic moment of the cluster randomly frozen.

Keywords : Ferrite, a.c. susceptibility, magnetization, canting angle

PACS Nos. : 75.30.Cr, 75.50.Gg

1. Introduction

The appearance of various magnetic structure caused due to change in concentration of non-magnetic ions in different sub-lattices, make ferrites a very interesting material [1-4]. Among these, systems with spinel structure seem to be particularly attractive, as they allow a variety of magnetic disorders and frustration to be introduced. Recently, a tentative phase diagram has been proposed [1] to classify the different substituted ferrite compounds. In addition to these, the presence of Mn^{4+}, Co^{2+} and Fe^{3+} in the ferrite system, introduce additional factors *i.e.* uniaxial random anisotropy [5], which increases the possible magnetic structure and changes the above mentioned phase diagram [1].

A large number of investigators have studied Ti - substituted spinels in order to understand their magnetic properties. Brand *et al* [6] have found in the case of $Mg_{1+x}Ti_xFe_{2-2x}O_4$ that on increasing dilution x, the collinear ferrimagnetic phase breaks down before reaching the ferrimagnetic percolation threshold and for higher concentration of Ti system approaches towards spin glass. Dormann *et al* [7] have also studied the magnetization measurements of Ti^{4+}- substituted lithium ferrite using different techniques and suggested the possibility of canted spin arrangement to explain the magnetization measurements.

* Corresponding Author

In order to understand the influence of magnetic ion Mn^{4+} in place of nonmagnetic Ti^{4+}, we have carried out structural and magnetic measurements on Zn-substituted $Co_{1+x}Mn_xFe_{2-2x}O_4$ system.

Our results on $Co_{1+x}Mn_xFe_{2-2x}O_4$ system show that Mn^{4+} and Co^{2+} ions occupy B-sites while A-site is mainly occupied by Fe^{3+} ions. The magnetization results show collinear spin arrangement for $0 \le x \le 0.3$. The temperature dependent a.c. susceptibility measurements $[\chi_{ac}(T)]$ results of $Co_{1+x}Mn_xFe_{2-2x}O_4$ system display two peaks, one sharp near $T_N \sim 605$ K and another broad peak at much lower temperature $T_f \sim 450$ K. The $\chi_{ac}(T)$ behaviour observed in this system, can be explained using the magnetic phase diagram proposed for the disordered spinel system [8] and according to which the existence of two peaks up to $x < 0.5$ indicate that the system undergoes a para to unstable ferromagnetic transition (T_N) followed by cluster spin glass ordering (T_f). We have modified the ferromagnetic phase of $Co_{1.5}Mn_{0.5}FeO_4$ ($x = 0.5$) by substituting magnetic Co^{2+} (3mB) ions with non-magnetic Zn^{2+} ions with non-magnetic Zn^{2+} ions in the system. Thus, the magnetic ion concentration of the A sub-lattice reduces, which may lead to frustration in the sub system. In view of this, bulk magnetic properties of the $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ system have been investigated for $x \le 0.6$. Here we report the results of X-ray

diffraction, magnetization and a.c. susceptibility measurements on the above spinel system.

2. Experimental

Seven samples of the spinel series $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ with x = 0.0 to 0.6 were prepared by the usual double sintering ceramic process. The starting materials were analytical reagent grade oxides, Fe_2O_3, ZnO, MnO_2 and CoO. These oxides were mixed in proper proportions and pre-sintered at 900°C for 12 hours. In the final sintering process, the material was held at 1100°C for 12 hours for complete ferritization and then slowly cooled at room temperature at the rate of 2°C / minute. The X-ray diffractograms were recorded using CuKa radiation on a Philips X-ray diffractometer (PW 1700). The diffraction pattern showed sharp lines corresponding to a single-phase spinel structure for all samples (Figure 1).

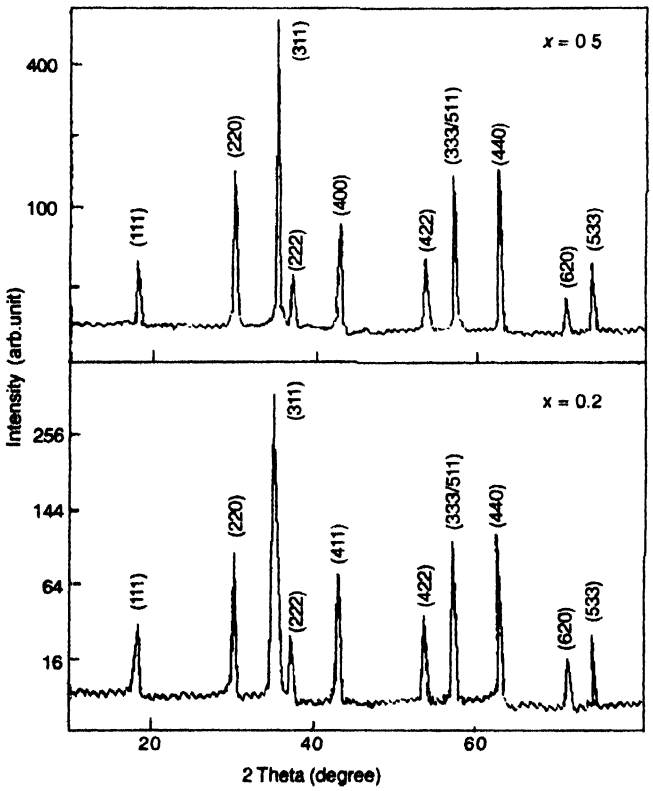

Figure 1. Typical X-ray diffraction pattern of Co-Mn-Fe-O ferrite.

Room temperature (300K) magnetization measurements were performed using high field hysteresis loop technique [9]. Low field a.c. susceptibility measurements were carried out using a double coil set up as described elsewhere [10] in the temperature range of 77 to 600 K. The applied field was 0.5 Oe.

3. Results and discussion

Figure 1 depicts typical X-ray diffraction patterns for $x = 0.2$ and $x = 0.5$. The lattice constant 'a' (Å) of the series $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ plotted as a function of 'x' is shown in Figure 2. It is observed from Figure 2. that the lattice constant 'a' (Å) increases with Zn content 'x'. The variation of lattice constant 'a' (Å) with Zn content 'x' can be explained on the basis of difference in ionic radii of constituent ions. The increase in lattice constant 'a' with 'x' is due to the fact that the larger Zn^{2+} (0.74 Å) ions replace smaller Co^{2+} (0.71 A0) ions in the spinel

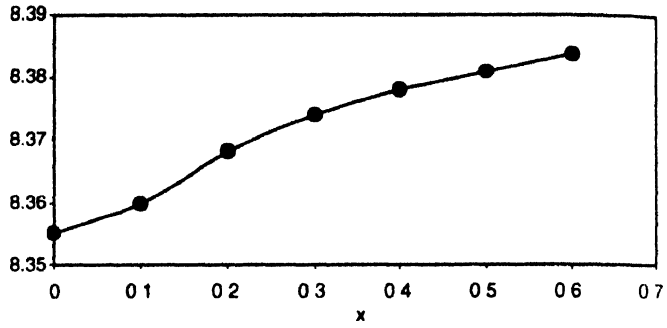

Figure 2. Variation of lattice constant with x.

lattice. This behaviour is similar to the Zn^{2+} substituted Co-Ge [11], and Co-Ti [8] system, in which lattice constant 'a' (Å) increases with concentration 'x'. Comparing the site preference energies of the constituent ions [12] and from the earlier results [13], the cation distribution for $x = 0.0$ was found to be

$$(Fe)^A[Co_{1.5}Mn_{0.5}]^B O_4^{-2}.$$

In order to determine the cation distribution for the substituted system, the X-ray intensity calculations were made using the formula suggested by Burger [14]

$$I_{hkl} = |F_{hkl}|^2 . P . L_p,$$

where, F_{hkl} is the structure factor, P is the multiplicity factor and L_p is the Lorentz polarization factor. It is known [15] that the intensity ratio of planes $I(220)/I(400)$, $I(220)/I(440)$ and $I(400)/I(422)$ are considered to be sensitive to the cation distribution parameter (x); therefore, these ratios are used in estimating the cation distribution. As Zn^{2+} ions have strong preference for A-site, cation distribution for the present system can be written as

$$(Zn_xFe_{1-x})^A[Co_{1.5-x}Fe_x]^B O_4^{-2}.$$

Finally, the cation distribution for these compounds is estimated from magnetization (300 K) and X-ray intensity calculations. Table 1 gives the results of X-ray intensity calculation for the best-fit cation distribution for $x = 0.1, 0.2, 0.3$, and 0.5 samples.

The saturation magnetization (σ_s) and the magneton number (n_B) (the saturation magnetization per formula unit in Bohr magneton) at 300 K obtained from magnetization data for all the samples up to $x = 0.4$ are summarized in Table 2. Figure 3 shows the variation of n_B with Zn-content (x). It is evident from Figure 3 that n_B increases upto $x < 0.3$ and then decreases. From eq. (2), it is clear that as Zn replaces the magnetic ions from A-site, the

Table 1. Comparison of X-ray intensity ratios for $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$

Content x	A-site cation	B-site cation	$I_{(220)}/I_{(440)}$		$I_{(220)}/I_{(400)}$		$I_{(400)}/I_{(422)}$	
			Obs	Cal	Obs.	Cal.	Obs	Cal
0.1	$(Zn^{2+}_{0.1}Fe^{3+}_{0.9})$	$(Co^{2+}_{1.4}Mn^{4+}_{0.5}Fe_{0.1})$	0.660	0.631	1.260	1.164	1.920	2.500
0.2	$(Zn^{2+}_{0.2}Fe^{3+}_{0.8})$	$(Co^{2+}_{1.3}Mn^{4+}_{0.5}Fe_{0.2})$	0.800	0.602	1.190	1.400	2.460	2.050
0.3	$(Zn^{2+}_{0.3}Fe^{3+}_{0.7})$	$(Co^{2+}_{1.2}Mn^{4+}_{0.5}Fe_{0.3})$	0.730	0.661	2.000	1.340	1.720	2.150
0.5	$(Zn^{2+}_{0.5}Fe^{3+}_{0.5})$	$(Co^{2+}_{1.0}Mn^{4+}_{0.5}Fe_{0.5})$	1.050	0.691	2.150	1.700	1.430	1.670

Table 2. Saturation magnetization (σ_s), magneton number (n_B), Yafet - Kittel angle (α_{YK}) and Curie temperature (T_c) for the $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ system [17].

The exchange constants used in calculating α_{YK} are

$J_\alpha = -15$ K, $J_\beta = -5$ K, $J_\gamma = -14$ K, $J_\delta = -9$ K, $J_\varepsilon = -4$ K, $J_\xi = -7.5$ K, $J_\sigma = -7.5$ K, $J_\psi = -12$ K, $J_\mu = -4.5$ K

Zn-Content	σ_s (emu/gm) 300 K	n_B (μ_B)	α_{YK} (Obs) In degrees	α_{YK} (Cal)	T_c (K) (±5K)
0.0	33.60	1.41	-	-	458
0.1	34.07	1.44	-	-	428
0.2	40.06	1.70	34.30	41.46	403
0.3	34.25	1.45	45.80	42.09	383
0.4	22.89	0.97	57.05	59.97	360
0.5	-	-	-	-	318
0.6	-	-	-	-	300

magnitude of the A-site moment decreases but the difference between A-site and B-site moments increases; as a result, the nB increases. Therefore, the initial increase in n_B with x can be explained with eq. (2); but the decrease in n_B after x > 0.3 indicates the possibility of a non-collinear spin structure in the system. On account of the similarities between the present system and the other Zn-substituted system [11], it is reasonable to assume Yafet-Kittel (Y-K) [16] type magnetic ordering in the present system.

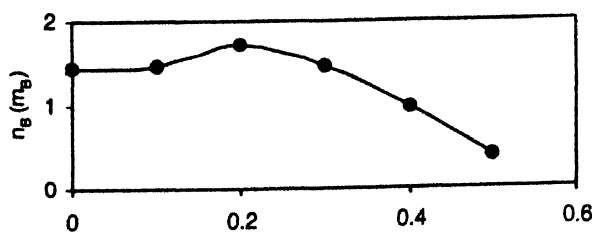

Figure 3. Variation of a. c. susceptibility with x.

Adopting the procedure of Satyamurthy *et al* [2], the condition for the existence of a Y-K angle can be found for $x \geq 0.2$. Using this model [2], the part of interaction energy 's' involving Y-K angle may be written as

$$E(YK) = [15(1-x)(1.5-x)\alpha + 25(1-x)x\beta + 20(1-x)(0.5)\gamma]$$
$$\times \cos(\alpha_{YK})^{-1/4}[9(1.5-x)^2\delta + 30(1-x)(1.5-x)\varepsilon + 25x^2\xi$$
$$+40x(0.5)\sigma + 24(1.5-x)(0.5)\psi\ 16(0.5)\,2\mu]\cos(2\alpha_{YK})],$$

where $\alpha, \beta, \gamma, \delta, \varepsilon, \xi, \sigma, \psi$ and μ are the molecular field constants related to the following sets of interactions:

$$\alpha : A(Fe^{3+}) - B_1(Co^{2+}),$$
$$\beta : A(Fe^{3+}) - B_1(Fe^{3+}),$$
$$\gamma : A(Fe^{3+}) - Bi(Mn^{4+}),$$
$$\delta : B_1(Fe^{3+}) - B_2(Co^{2+}),$$
$$\varepsilon : B_1(Fe^{3+}) - B_2(Co^{2+}),$$
$$\xi : B_1(Fe^{3+}) - B_2(Fe^{3+}),$$
$$\sigma : B_1(Mn^{4+}) - B_2(Fe^{3+}),$$
$$\psi : B_1(Co^{2+}) - B_2(Mn^{4+}),$$
$$\mu : B_1(Mn^{4+}) - B_2(Mn^{4+}).$$

The energy is minimum for either

(a) $\sin(\alpha_{YK}) = 0.0$ which corresponding to Neel's configuration,

or

$$\text{(b)}\cos(\alpha_{YK}) = \frac{[15(1-x)(1.5-x)\alpha + 25(1-x)x\beta + 20(1-x)(0.5)\gamma]}{[9(1.5-x)^2\delta + 30(1-x)(1.5-x)\varepsilon + 25x^2\xi + 40x(0.5)\sigma + 24(1.5-x)(0.5)\psi\ 16(0.5)2\mu]} \quad (1)$$

which corresponds to the situation where the Y-K angle is feasible. The molecular constants can be obtained from the variation of saturation magnetization with Zn content. The

experimental values of α_{YK} can be obtained from the observed variation of n_B with x using the relation [16]

$$n_B = M_B \cos(\alpha_{YK}) - M_A, \quad (2)$$

where M_B and M_A are the magnetic moments of B-sites and A-sites respectively. Table 2 contains the values of α_{YK} obtained using eqs. (3) and (4). The experimental values of α_{YK} agree nearly well with those obtained theoretically. This suggests that in this system, AB and BB super-exchange interactions are complete in strength.

Figure 4 shows the plots of thermal variation of a.c. susceptibility (χ_T/χ_{RT}), for all the samples, which exhibit normal ferrimagnetic behaviour. It can be seen from Figure 4 that all the samples, only one peak is observed and on increasing Zn concentration x, the peak shifts towards lower temperature. The intensity of this peak decreases with increase in Zn concentration x.

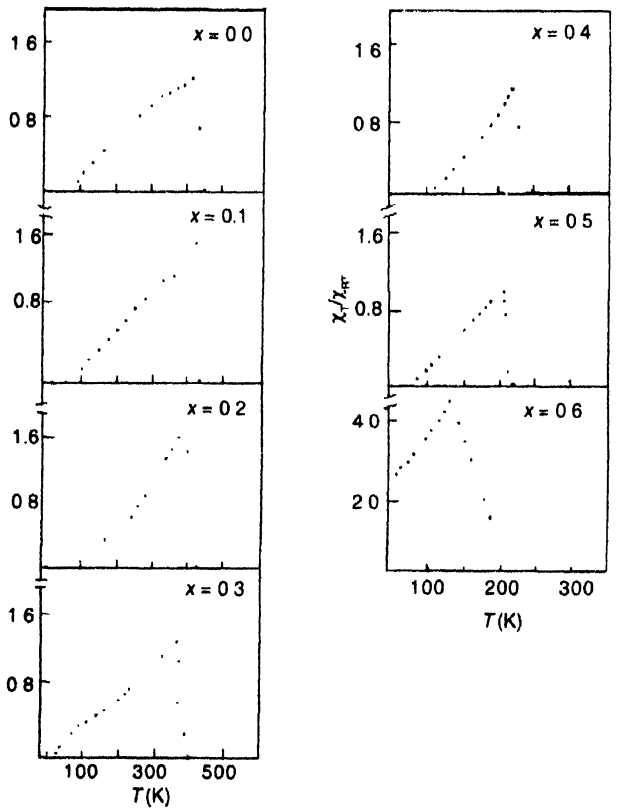

Figure 4. Thermal variation of a. c. susceptibility.

The values of Curie temperature (T_c) deduced from χ_T/χ_{RT}-plots are summarized in Table 2. According to Neel's model, A–B interaction is most dominant in ferrites; therefore, Curie temperature of the ferrites are determined from the overall strength of A–B interaction. The strength of A–B interaction is a function of the number of $FeA^+ - O^{2-} - Fe\ B^{3+}$ linkages, which in turn, depends upon the number of Fe^{3+} ions in the formula unit and their distribution amongst tetrahedral (A) and octahedral [B] sites. In the present system, Co^{2+} ions ($3\mu_B$) are replaced by Zn^{2+} ions ($0\mu_B$). This results in decreasing the A-B interaction which lead to decrease in Curie temperature (T_c)

4. Conclusion

In conclusion, our X-ray diffraction, magnetization and a.c susceptibility measurement on the disordered spinal system $Co_{1.5-x}Zn_xMn_{0.5}FeO_4$ show that

(i) Mn^{4+} and Co_{2+} ions occupy B-site only, Zn^{2+} have strong A-site preference and Fe^{3+} ions distributed among A- and B-sites.

(ii) Magnetization results exhibits a significant canting on the B-site which is satisfactorily explained on the basis of uniform canting model.

(iii) a.c. susceptibility data indicates that T_c decreases with increasing concentration x.

References

[1] J L Dormann and M Nognes *J Phys. Condens. Matter* **2** 1223 (1990)

[2] N S Satyamurthy, M G Natera, S I Youssof, R J Begum and C M Srivastava *Phys. Rev.* **181** 4412 (1269)

[3] D Fiorani, S Viticoli, J L Dormann, J L Tholence and A P Murani *Phys. Rev.* **B30** 2776 (1984)

[4] K Murlidharan, J K Srivastava, V R Maratna and R Vijayraghavan *J. Phys.* **C18** 5897 (1985)

[5] J B Goodenough *Magnetism of the Chemical Bond* (New York Wiely) (1963)

[6] R A Brand, Georges H Gilbert, H Hubsch and J A Hellei *J Phys* **F15** 1987 (1985)

[7] J L Dormann, M El Harfaouni, M Nogues and J Love *J Phys* **C20** L161 (1987)

[8] R V Upadhyaya, R B Jotania and R G Kulkarni *Physica* **B190** 183 (1993)

[9] C Radhakrishna Murthy, S D Likhate and S Sastry *Phil. Mag* **23** 803 (1971)

[10] C Radhakrishna Murthy, S D Likhate and P W Sahastrabudhe *Proc. Indian. Acad Sci.* **87** A245 (1978)

[11] R B Jotania, R V Upadhyaya and R G Kulkarni *IEEE Trans Magn.* **28** 1889 (1992)

[12] D Fiorani and S Vitcoli *Solid State Commun.* **29** 1363 (1978)

[13] D R Shengule, *Ph. D. Thesis* (Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India) (1999)

[14] M J Burger *J. Crystal Structure Analysis* (New York : John Wiley) (1960)

[15] H Ohnishi and T Teranijhi *J. Phys. Soc. Jpn.* **16** 36 (1961)

[16] Y Yafat and C Kittel *Phys. Rev.* **87** 290 (1952)

[17] F Scholl and K Binder *Z. Phys.* **B39** 239 (1980)

[18] C M Shrivastava, S N Shringri, R G Shrivastava and N G Nanandikar *Phys. Rev.* **B14** 2032 (1976)